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Investigation into the Morphology, Composition, Structure and Dry Tribological Behavior of Rice Husk Ceramic Particles

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Abstract：

To expand the application of rice husk (RH) resource, this study developed carbon-based RH ceramic (RHC) particles using a common high-temperature carbonization method. The morphology, composition, and structure of the RHC particles were characterized with a series of modern analysis technologies and were then compared with those of the initial RH powder and carbonized RH (CRH) particles. The dry tribological behavior of RHC particle adobes (RHAs) was also investigated. Results showed the sheet-shaped morphology of the RHC particles. The graphitization degree of the RHC particles was lower than that of the CRH particles possibly because the phenolic resin (PR) filled the micro-pores of the RH particles, thereby prompting the formation of amorphous carbon in the RHC particles as a result of high-temperature carbonization. The appearance of a hydroxy function group (–OH) on the surface of the RHC particles was ascribed to the decomposition of PR at 900 °C. The friction coefficients and mass loss rates of the RHAs almost increased with the rise in load and velocity. In addition, the friction coefficients of the RHAs decreased at high load (5 N) and velocity (0.261 m/s) conditions. Such outcome indicated that the variation of contact area between steel ball and RHA at high load and velocity conditions resulted in the abrasive wear or catastrophic wear.

Keyword: Rice husk ceramic particles, Morphology, Composition and structure, Dry friction

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1. Introduction

The comprehensive utilization of biomass resources has received increasing attention as a solution to the serious environment, resource, and energy crises. In China, the acreage of crops is approximately 145 million ha per year. Food crops comprise 76% of the total acreage, with rice yield amounting to approximately 400 million; such large amount of rice yield can in turn produce a considerable amount of rice husks (RHs), which could induce a security crisis, such as burning and storage issues **[1–2]**. The firing of RHs in farms releases pollutants that adversely affect the environment. Therefore, the comprehensive utilization of RHs is especially important. The preparation of rice husk ceramic (RHC) particles is a good method to conveniently utilize RHs. RHC can be used as a sliding element in linear guides and linear sliders because of its low Young's modulus, low friction coefficient, and high abrasion resistance.

The preparation of RHC particles has been extensively reported. For example, **Asano [3]** found that the 25% impregnation rate of phenol resin (PR) is the best dosage for promoting the mechanical properties of RH silicon carbon materials. **Unuma [4]** prepared a glass-like carbon/silicon material by co-carbonizing RH and PR in a nitrogen atmosphere at 900 ℃. In this work, inorganic constituents such as K_2O, SiO_2, NaO, and CaO were investigated and found to be the cause of the hygroscopic expansion of the carbonized material. However, the study did not examine the morphology and structure of the glass-like carbon/silicon material. **Kubo [5]** optimized the manufacturing processes of RHC particles to reduce the amount of inorganic constituents and consequently enhance the mechanical strength and hydrophobic properties of RHC materials. **Iizuka [6]** developed a new porous carbon material by mixing defatted rice bran

with PR. The study compared three types of manufacturing processes for preparing the porous carbon material with high mechanical properties. **Kumagai [7]** investigated a carbon/silica composite fabricated from RHs by means of binderless hot-pressing. The sintering temperature and size of the RH powders significantly influenced the bulk density of the carbon/silicon composite. The methods used in the aforementioned studies are extensively reported, but the morphology, composition, and structure of RHC particles have not received the same attention. In particular, few studies have explored the particles of carbonized rice husk (CRH) powders relative to RHC particles despite the potential benefits of CRH particles.

The morphology, composition, and structure of RHC particles determine the variation in their tribological behavior. **Dugarjav [8]** investigated the tribological behaviors of RHC with different friction pairs, such as high carbon chromium steel, austenitic stainless steel, and Al_2O_3, under dry conditions using a ball-on-disk tribometer. They found that the anti-friction and anti-wear properties of the RHC resulted from the film formation on the steel balls. However, the same was not detected for A_2lO_3, hence the high friction coefficient (0.14–0.23). The study also investigated the effect of carbonization temperature (900 °C, 1,400 °C, and 1,500 °C) on the tribological performance of the RHC and found 900 °C as the best carbonization temperature **[9]**. However, research on the effects of load and velocity on the tribological behaviors of RHC adobes (RHAs) remains limited. In the present work, we design a series of system tribological tests to investigate the dry tribological behaviors of RHAs under different load and velocity conditions. The results of this study can serve as a reference for the proper utilization of RH resource and can further enrich the tribological theory of carbon materials.

2. Experimental

2.1. Materials and apparatus

Commercially available RH powder (mesh size, 10) and PR (Model 2133) were purchased from the Yuanyang Yanbing Rice Industry Co., Ltd. and the Wuxi Mingyang Adhesive Material Co. Ltd., in China, respectively. The detailed processes of preparing the RHC particles and RHAs were shown in **Figure 1(a)**. Exactly 2.5 g PR was added to 7.5 g RH powder. The mixture was then stirred using a glass rod for 15 min. The 3 g mixture was transferred to a porcelain burning boat in a tube furnace (model OTF-1200X) at 900 °C and N_2 atmosphere conditions for 2 h and was then cooled at room temperature. The remaining powder comprised the RHC particles. The CRH particles were obtained with the same direct carbonization method applied to the RH powders. The RHAs were prepared via compression molding, as shown in **Figure 1(a)**. The mass ratio of the RHC particles and PR was 3:1.

2.2. Analysis methods

The internal structure and primary particles of the RHC and CRH were analyzed via high-resolution transmission electron microscopy (HRTEM, JEOL–2010) with a JEOL JEM-2010 system at an acceleration voltage of 200 kV. A drop of ethanol solution containing CRH or RHC particles was dropped onto the HRTEM Cu grids. The Cu nets were supported by thin carbon films.

Scanning electron microscopy with energy dispersive spectroscopy (SEM/EDS, model JSM-6700F) was employed to investigate the agglomerated morphology of three types of materials (RH, CRH, and RHC) and their fundamental element contents. The particle size distributions of the RH, CRH, and RHC were measured using a laser particle size analyzer (Model JL9200 SKL07). The surface chemical functional groups of the three types of carbonaceous

materials and the PR were analyzed with Fourier transform infrared spectroscopy (FTIR, Nicolet 6700 model).

An x-ray diffraction (XRD) analysis of the three types of carbonaceous materials was conducted using a Rigaku D/max-γB X-ray diffractometer with Cu-Kα radiation (λ = 1.542 Å). The average stacking height of graphite crystallite in the direction of *c* axis was determined with the following Debye–Scherrer equation **[10, 11]**:

$$L_{C(002)} = \frac{K\lambda}{\beta_{002}\cos\theta_{002}} \quad (1)$$

Where $L_{c(002)}$ is the average stacking height of crystallites in the direction of the *c* axis (nm), K is the shape factor (with a typical value of about 0.89), λ is the Cu X-ray wavelength (0.1542 nm), θ_{002} is the Bragg diffraction angle and β_{002} is the peak width of the diffraction peak profile at half maximum height.

Raman spectroscopy (LabRAM-HR, resolution = 0.6 cm^{-1}, scanning repeatability = ±0.2 cm^{-1}) was employed to investigate the carbon structure of the three particle types. For the powder samples, a dense layer approximately 1 mm thick was pressed with a steel spatula onto a silicon wafer, which was then placed on the microscope sample holder. The filtered samples and graphite bar were placed directly on the sample holder. The microscope was focused onto the sample surface with a white light source at 50× magnification. The white light was then replaced with a laser beam (532 cm^{-1}), and the Raman spectra were recorded (Stokes Raman shift = 100–3,500 cm) **[12]**. The microcrystalline graphitic planar size (L_a) of carbonaceous material is defined using the following formula **[13]**:

$$L_a = \frac{4.4}{\left(I_D/I_G\right)} \quad (2)$$

Where I_D and I_G are the integrated intensity of the G and D modes, respectively; L_a is microcrystalline graphitic planar size (L_a) of carbonaceous material, (nm).

The I_D/I_G rate reflects the degree of graphitization disorder of the carbonaceous material. The

wear resistance and friction reduction properties of the RHAs were assessed via a series of systematic tribological tests conducted under a controlled atmosphere using a micro-tribometer (WTM-2E model), which can be used to investigate the low load conditions of tribological tests **[14]**. **Figure 1(b)** shows the schematic diagram of the tribo-meter. The test temperature and relative humidity were approximately 25 °C and 60% (RH), respectively. The effects of load and velocity on the dry friction property of the RHAs were investigated. The upper tribological specimen was a stainless steel (grade 304) 5 mm diameter ball with a surface roughness was 0.35 μm (Ra) and a hardness of 74.0 (HRC). The lower specimens was RHA. The shore hardness of RHAs test pieces was 31-34 HS, measured with a shore hardness tester (Model HS-19A). The surface roughness of the RHAs was approximately 1.60 μm measured using a 3D laser scanning microscopy (mode VK-X100K). Each tribological test was conducted three times to reduce experimental deviation.

3. Results and discussion

3.1 Morphology analysis

Figure 2 shows the SEM images of the RH, CRH, and RHC particles under different magnifications. Micro-holes were observed in the RH particles (red rectangle in **Figure 2(a)**), but they were non-existent after the carbonization process at 900 °C (**Figure 2(b)**). The size of the RHC particles was obviously reduced compared with that of the RH and CRH particles, as proven in the analysis of the size distributions of the particles (**Figure 3**). The average particle sizes (APS) of the RH, CRH, and RHC particles were 408.2, 193.8, and 76.2 μm, respectively. In addition, the RHC particles were shaped like a sheet, as shown in **Figures 2(c)** and **4(c)**. These results indicated that PR could promote the variation in the morphology of the RH particles during the

carbonization process. The variation mechanism was ascribed to the PR added into the micro-holes of the RH particles, which were then subjected to carbonization at 900 °C to transform them into amorphous carbon[15]. The graphitization degree of the RHC particles was slightly lower than that of the pure CRH particles, as denoted by the yellow rectangle shown **in Figure 4(b)**. Graphite fragments appeared in the CRH particles. Their presence can be clarified with the electron diffraction diagrams of CRH and RHC in **Figures 4(b) and (d)**, respectively.

3.2 Composition and structure analyses

Figure 5 shows the EDS analysis spectra of the RH, CRH, and RHC particles. The main elements of the RH particles were C, Si, O, and K. The elements C, Si, O, Fe, Ca, and K were detected in the CRH particles [16]. The RHC particles only comprised C, O, and Si; its Fe, K, and Ca content was too low to be detected.

Figure 6 shows the Raman analysis spectra of the RH, CRH, and RHC particles. For the RH particles, two peaks at 1,300 and 2,880 cm^{-1} were attributed to the presence of organic compounds such as lignin and cellulose. The Raman spectra of the CRH and RHC particles both show that the two peaks at 1,326 and 1,580 cm^{-1} were attributed to the D and G peaks [17–19]. The I_D/I_G value (3.43 in **Table 1**) of the RH particles was lower than that of the RHC particles (I_D/I_G, 3.64). Hence, the degree of graphitization disorder of the RHC particles was slightly higher than that of the RH particles. These results are consistent with those of the HRTEM analysis shown in **Figures 4(b)** and **(d)**.

Figure 7 shows the XRD patterns of the RH and RHC particles. The peak at 22.01° was the crystal face (002) of graphite, thereby revealing the existence of a graphite micro-crystal. The three peaks at 20.08°, 22.01°, and 42.38° were attributed to the 002 crystal faces of SiO_2 and the

002 and 101 crystal faces of graphite according to the standard card PDF41-1487 database **[20, 21]**. The corresponding average stacking height of crystallite in the direction of *c* axis of the RH, CRH, and RHC particles were approximately 1.61, 3.08, and 5.31 nm, respectively (**Table 1**). The $L_{c(002)}$ (5.31 nm)of RHC particles was higher than that of CRH (3.08 nm) particles. However, the microcrystalline graphitic planar size (L_a) of RHC（1.20 nm）was smaller than that of CRH (1.28 nm). Moreover, the degree of graphitization disorder of the RHC particles (3.64) was higher than that of the CRH particles (3.43) which indicated the ordered graphitization carbon content of RHC was lower. These phenomena indicated that some components of the RH particles were lost during the carbonization process, with the remaining components being amorphous carbon and silicon dioxide. The crystallite size of silicon dioxide was approximately 81.05 nm. Moreover, the 002 peak of the RHC particles was weaker than that of the CRH particles, thereby indicating that the graphitization degree of the CRH particles was higher than that of the RHC particles.

Figure 8 shows the FTIR analysis of the RH, RHC, and CRH particles. For the RH particles, the peaks at 3,438, 2,926, 2,844, 1,624, and 1,093 cm^{-1} were attributed to the –OH stretching vibration, $–CH_3$ and $–CH_2–$ stretching vibration, C=C stretching vibration, and Si–O stretching vibration **[22–25]**. For the CRH particles, the peaks at 3,438, 2,926, and 2,826 cm^{-1} almost disappeared. Hence, the components of the RH particles were completely decomposed at 900 °C, except for the silicon compound, the presence of which was demonstrated by the peak at 683 cm^{-1} (Si–O bending vibration). The absent peaks were detected when PR was added into the RH particles. In addition, the peaks at 3,438 cm^{-1} (–OH), 1,624 cm^{-1} (C=C), 1,093 cm^{-1} (Si–O stretching vibration), and 683 cm^{-1} (Si–O bending vibration) intensified. These results were ascribed to the introduction of the PR, which caused the chemical reactions between the RH

powder and PR **[25, 26]**.

3.3 Tribological performance

Figures 9 (a) and **(b)** show the friction reduction property of the RHA at different load and velocity conditions for 30 min. The friction coefficients almost increased with the rise of load and velocity. However, the friction coefficients decreased under velocities of 0.261 and 0.157 m/s with stationary loads at 2 and 5 N, respectively.

Figures 9 (c) and **(d)** show the wear resistance property of the RHAs under different load and velocity conditions for 30 min. The effect of velocity on the wear resistance of the RHAs was more obvious than the effect of load conditions. The highest mass loss rate was observed at a load of 2 N and a velocity of 0.209 m/s (**Figure 9(c)**). Moreover, the mass loss rate of the RHAs almost increased as the velocity and load increased.

Figures 10 shows the variation of the full-scale surface morphologies of RHAs after friction testing at different load and velocity conditions. The width of wear traces increased with the increases of load and velocity. In particular, catastrophic wear appeared when the velocity was 0.209 m/s and load was 2 N.

Figures 11 and **12** show the cut-off worn surface profiles and corresponding surface roughness of the worn surfaces of the RHAs. The width of the wear traces almost increased at high load and velocity conditions. However, the width of the wear traces decreased when the velocity increased to 0.105 or 0.261 m/s at 2 N for 30 min. Besides, The surface roughness of the wear traces also decreased from 167.49 μm (0.209 m/s) to 71.92 μm (0.261 m/s), as shown in **Figures 11 (e')** and **(f')**. The results are consistent with the variations in the friction coefficients and mass losses shown in **Figures 9(a)** and **(c)**. As for the effect of load, the width and surface

roughness of the wear traces almost increased as the load increased, except when the load was 4 N (**Figure 12(e)**).

3.4 RHC particle formation and friction mechanism analysis

The PR first filled the micro-caves of the RH powder during the preparation process, and the components of the mixture easily decomposed at 900 °C for 2 h. The thermosetting PR disintegrated into small organic molecules at a high temperature. These organic molecules can also react with the RH powders to form amorphous carbon materials. Thus, the graphitization degree of RHC particles was lower than that of the CRH particles. In addition, small organic molecules, including the –OH group, could be adsorbed on the surface of the RHC particles, thereby improving the intensity of the peak at 3,436 cm^{-1} of the FTIR analysis.

The wear of RHAs became serious at high load and velocity conditions. Abrasive wear resulted in a dramatic increase of the wear track width and depth. The increase of both load or velocity resulted in the variation of apparent contact areas between steel ball and RHA as shown in **Table 2**. As a result of this, catastrophic wear appeared at 0.209 m/s and 2 N as shown in **Figure 10 (0.209 m/s) and Figure 11(e)**.

4 Conclusions

The common high-temperature carbonization method was employed to prepare RHC particles. The morphology, composition, and structure of the RHC particles were characterized using a series of modern analysis technologies. The tribological behavior of the RHAs was also investigated using a micro-tribometer under a controlled atmosphere. The following conclusions can be drawn:

(1) The RH particles exhibited a sheet-like morphology, as revealed by the SEM and

HRTEM analyses. The graphitization degree disorder of the RHC particles was lower than that of the CRH particles possibly because the PR filled the micro-pores of the RH and CRH particles, thereby promoting the formation of amorphous carbon in the RHC particles.

(2) The presence of the hydroxy function group (–OH) in the RH particles was attributed to the decomposition of the PR.

(3) The appearance of serious wear of RHAs was ascribable to the increase of apparent contact area between steel ball and RHAs, which resulted in abrasive wear or catastrophic wear at high load and velocity conditions.

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